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ESR STUDIES OF HMX PYROLYSIS PRODUCTS

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The decomposition species resulting from low pressure pyrolysis of HMX (cyclotetramethylene tetranitramine) near its melting point have been studied using electron spin resonance spectroscopy of low temperature matrices. The radicals CH_2N and NO_2 are observed below the melting point; only NO_2 is observed at higher temperatures. Possible primary thermal decomposition mechanisms that are consistent with the observations are discussed.

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I. INTRODUCTION

Although the thermal decomposition of the high explosive cyclic nitramines, cyclotetramethylene tetranitramine (HMX) and cyclotrimethylene trinitramine (RDX) has been studied for several years[1-5], interest has been reawakened by their recently found role as components of new gun propellants. Here we report the observations of radical species resulting from the slow pyrolysis of HMX near its melting point and interpret these results in terms of the mechanisms of thermal decomposition during ignition and combustion.

II. EXPERIMENTAL

A schematic diagram of the apparatus is shown in Figure 1. Military grade HMX was used both without purification and after recrystalization from acetone with no significant difference noted in the results. Pyrolysis samples were placed in a 5-mm pyrex tube attached to one port of the vacuum jacket of a cryogenic refrigerator. Three pyrolysis methods were used: (1) immersing the sample tube in a constant temperature sandbath, (2) heating the sample tube with a propane/air flame for one minute, resulting in melting and decomposition of the sample, and (3) heating with a 750W quartz iodine lamp. Temperature of the sandbath was monitored with a thermometer; when heating with the lamp the substrate temperature was measured with a thermocouple. No temperature measurements were made with flame heating. The gaseous pyrolysis products were mixed with argon entering the jacket from the opposite port at a flow rate of 1.62×10^{18} atoms/s. This mixture was then condensed as a solid matrix on the sapphire rod cooled to near 15K. Electron spin resonance (esr) spectra were then recorded for the radicals in the matrix.

III. RESULTS

Typical spectra observed with HMX at 260 and 270°C are shown in Figure 2. All absorption lines observed in these studies were assigned to NO_2 and CH_2N. Although they do not appear in this figure, all ten CH_2N lines were observed under flow and trapping conditions which tend

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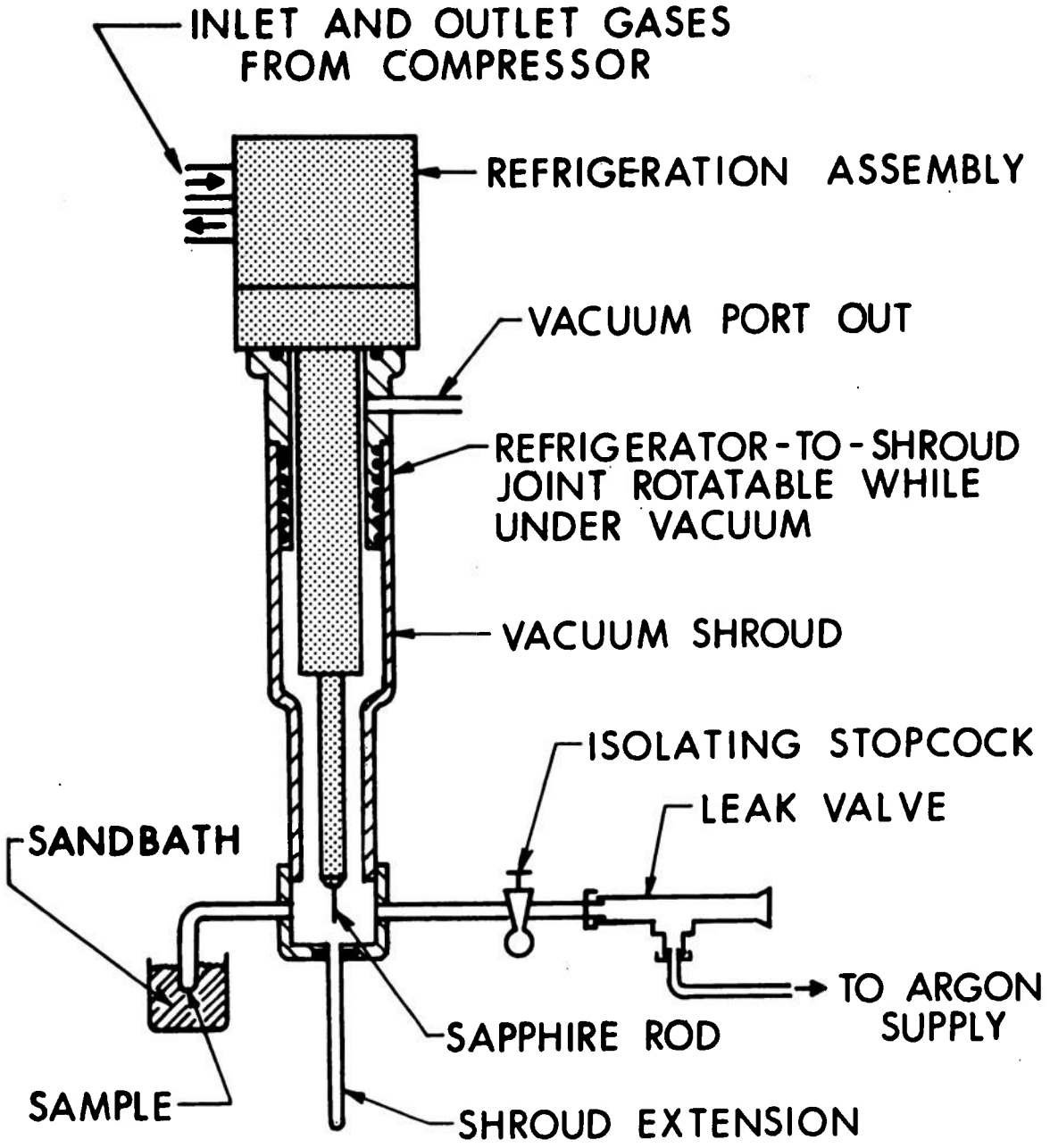

Figure 1. Schematic Diagram of Apparatus Used for Low Pressure Pyrolysis Studies. The material is pyrolysed in the sample tube. Resulting products are mixed with argon and frozen into a matrix at 20K on the sapphire rod for ESR studies of free radicals present.

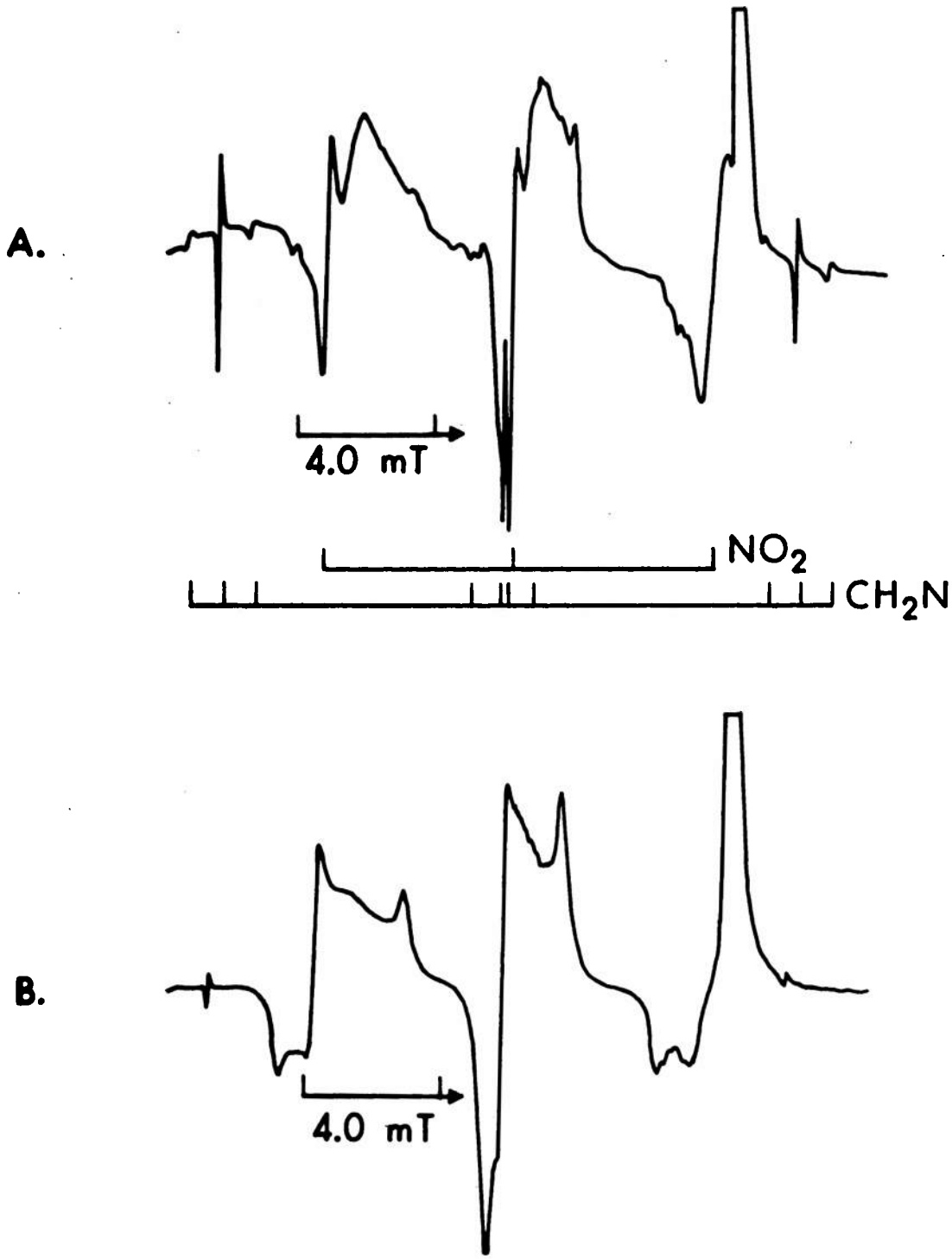

Figure 2. Spectra Observed for the Products of Pyrolysis of HMX at (A) 260°C and (B) 270°C.

to enhance the dimerization of NO_2. Figure 3 shows the ratio of NO_2 to CH_2N concentrations versus temperature for HMX pyrolysis and the relative CH_2N concentrations. The Figure shows that the ratio changes little at the lower temperatures but increases rapidly as the melting point is approached. The concentration of CH_2N shows an increase with temperature to a maximum near 260°C before disappearing near the melting point. The values of the ratios in this Figure do not include the differences in collection or detection sensitivity of the two species and should not be used in an absolute sense.

In the torch heating runs and in those sandbath runs above the melting point no CH_2N radicals were observed. Under these conditions, the NO_2 concentration, Figure 4A, was so great that the triplet radical pair spectrum[6] of $(NO_2)_2$ was observed at the half field position as shown in Figure 4B. In the quartz iodine lamp runs CH_2N and NO_2 appeared in amounts comparable to those from heating with the sandbath at the same temperature.

IV. DISCUSSION

A. ESR Spectra

The spectrum which we have assigned to CH_2N agrees with previous observations[7-10]. In the present work, the spectrum of the CH_2N radicals consisted of a triplet of triplets produced by the interaction of the two equivalent H atoms with the free electron (a_H = 8.40 ± 0.05 mT) with each of these lines further split into a triplet by the interaction with the nitrogen atom (a_N = 0.90 ± 0.05 mT). It was observed that the central line of the central triplet was also split into two lines due to a second order effect as was reported by Cochran, Adrian, and Bowers[7]. The observed g value for CH_2N was 2.0038 ± 0.0003. The triplet pair spectrum generated by the $(NO_2)_2$ species consisted of five lines with an intensity distribution 1:2:3:2:1 and nitrogen hyperfine splitting a_N = 2.77 mT.

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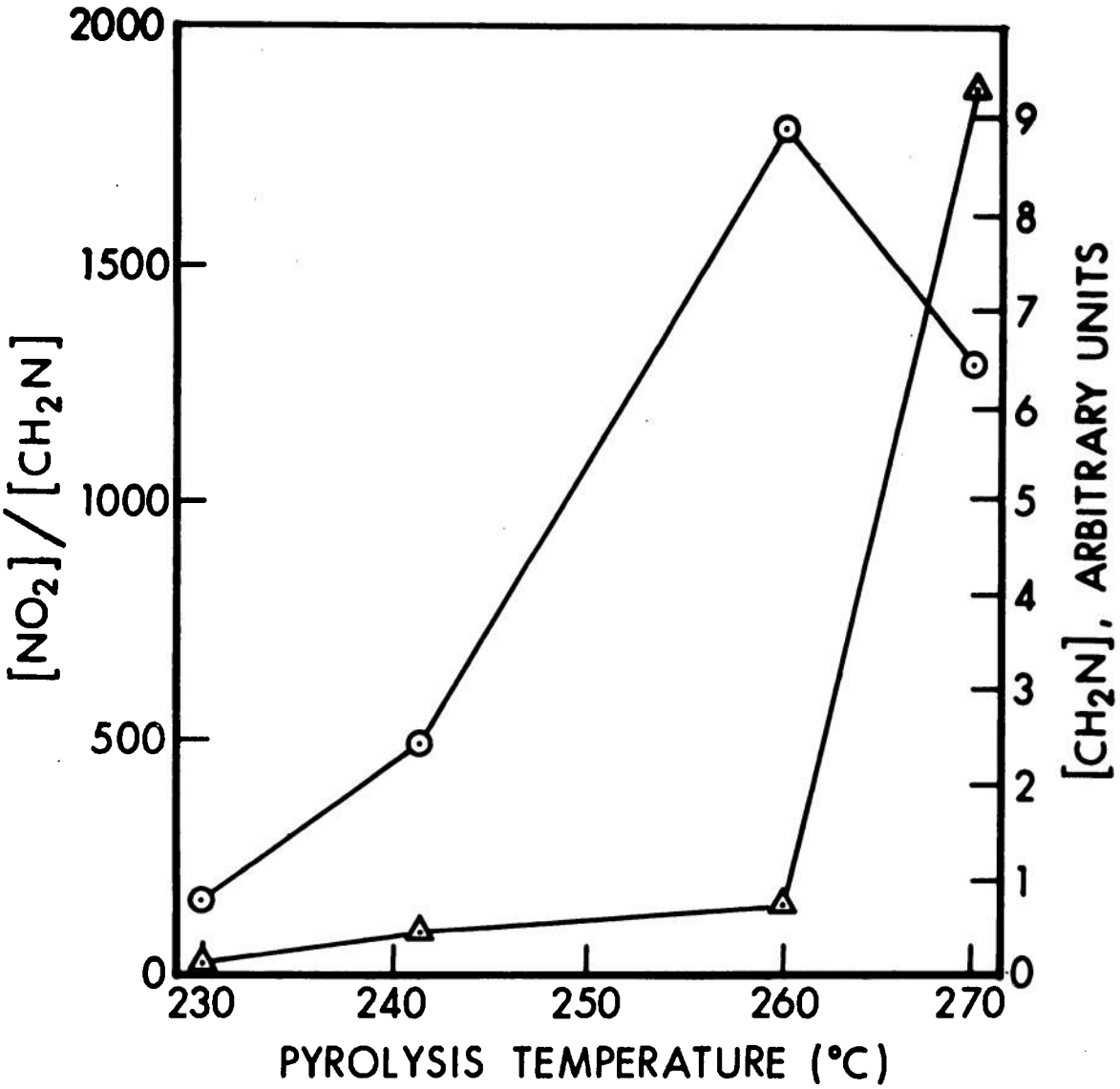

Figure 3. Concentrations of the Two Species Observed in HMX Pyrolysis; -0-. $[CH_2N]$ in Arbitrary Units, and -Δ-, Apparent Ratio of $[NO_2]$ to $[CH_2]$.

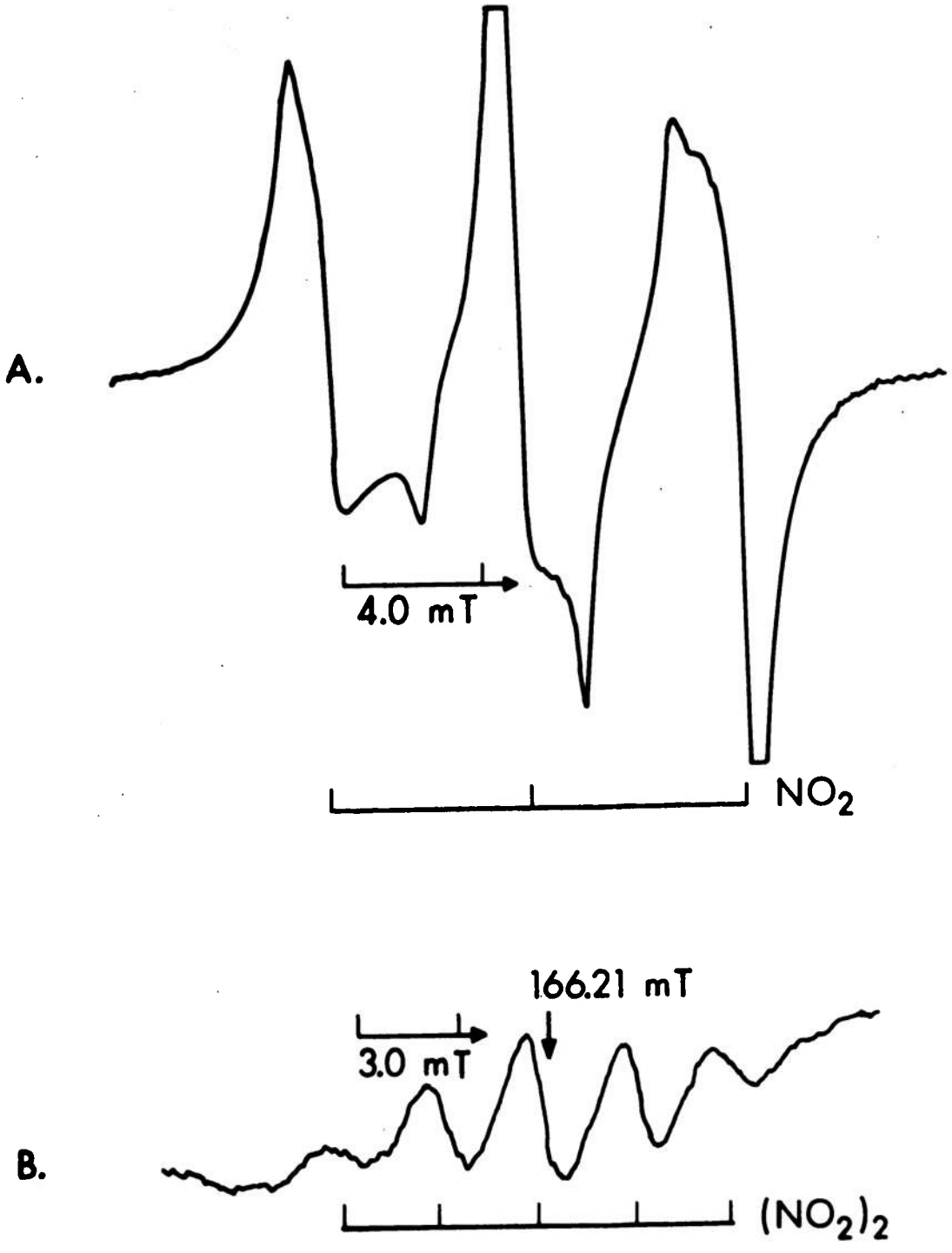

Figure 4. The ESR Spectra Resulting from HMX Pyrolysis Above Its Melting Point, Showing NO_2 (A) and $(NO_2)_2$ (B).

B. Mechanisms of Decomposition

Previous studies of the thermal decomposition of HMX below its melting point have been variously interpreted[11]. However, this present study is the first to find CH_2N. A possible source of CH_2N is the proposed[11] intermediate CH_2NNO_2 which should readily decompose thermally to NO_2 and CH_2N. This interpretation is supported by recent mass spectral studies[12] of the products of thermal decomposition of HMX near its melting point. That work shows a peak at 75-amu, identified as CH_3NNO_2, which is observed over essentially the same temperature range with similar intensity behavior as that shown in Figure 2 for CH_2N. Although it is possible to write other mechanisms which produce CH_2N such as proposed[13] in the mass spectral fragmentation of RDX, the present data do not require such additional sources. The change in observed species near the melting point might be interpreted as possible evidence for a change in decomposition mechanism upon melting of HMX. However, the reactive CH_2N should be expected to be depleted more rapidly than NO_2 in the melt or in gas phase reactions as the temperature of pyrolysis increases. Although this question must be answered by further observations, the substantial amounts of CH_2N should not be ignored in models of HMX thermal decomposition.

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